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(54) PROCESS FOR THE GAS-PHASE POLYMERIZATION OF OLEFINS

VERFAHREN FÜR DIE GASPHASENPOLYMERISATION VON OLEFINEN

PROCEDE DE POLYMERISATION EN PHASE GAZEUSE D'OLEFINES

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EP-A- 0 120 503 EP-A- 0 338 676

- **Encyclopedia of Polymer Science and Engineering, II Edition, Volume 13, pages 478, 488, 490 and 491**

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DescriptionField of the Invention

5 The present invention relates to a process for the gas-phase polymerization of olefins of the formula $\text{CH}_2=\text{CHR}$ in which R is hydrogen or an alkyl or aryl radical with 1 to 8 carbon atoms, which is carried out in one or more reactors having a fluidized or mechanically agitated bed, in the presence of a highly active catalyst comprising a titanium compound supported on active Mg-dihalide.

10 Background Information

It is known to continuously polymerize one or more olefins, such as ethylene or propylene, in the gas-phase in a reactor with a fluidized or mechanically stirred bed, in the presence of a catalyst based on a compound of a transition metal belonging to groups IV, V or VI of the Periodic Table of the Elements: in particular in the presence of a catalyst 15 of the Ziegler-Natta type or a catalyst based on chromium oxide.

The polymer particles are kept in the fluidized and/or stirred state in a gaseous reaction mixture containing the olefin(s). The catalyst is introduced continuously or intermittently into the reactor while the polymer constituting the fluidized or mechanically stirred bed is withdrawn from the reactor, also continuously or intermittently. The heat of the polymerization reaction is essentially removed by the gaseous reaction mixture which passes through heat transfer means before being recycled into the reactor. In addition, a liquid stream may be introduced into the gas-phase reactor to enhance heat removal.

When a process for the gas-phase polymerization of an alpha-olefin is carried out in the presence of catalysts of high activity, such as those formed of the product of the reaction of an Al-alkyl compound with a titanium compound supported on active Mg-dihalide, the problem of heat removal is increased due to the low capacity of heat exchange 25 of the gaseous phase.

It has been observed that small variations in the course of the polymerization, resulting, for example, from slight fluctuations in the quality of the catalyst or the olefins used in the reaction, can cause changes in the behavior and the catalytic activity of the polymer particles and have a particularly adverse effect because the small variations can cause an unexpected increase in the amount of heat evolved by the reaction which cannot be removed sufficiently rapidly and efficiently by the gaseous reaction mixture passing through the bed. Hot spots in the bed, as well as agglomerates of molten polymer, can be formed.

When hot spots appear in the bed it is generally too late to prevent the formation of agglomerates. However, if the reaction conditions are corrected sufficiently early, as by lowering the polymerization temperature or pressure, or reducing the rate at which the catalyst is supplied to the reactor in order to avoid the adverse effects of unexpected superactivation, the amount and size of the agglomerates formed can be reduced to some degree. During this period, however, it will not be possible to avoid a drop in the rate of polymer production and a deterioration in the quality of the resulting polymer.

To avoid these disadvantages, the general polymerization conditions are usually chosen with a safety margin such that hot spots and agglomerates do not form. For example, catalysts with reduced activity are used. The application of such conditions, however, either results in a substantial decrease in production or in a deterioration of the quality of the polymer.

To attempt to remedy the above drawbacks, EP 359444 A 1 discloses the introduction into the polymerization reactor of a retarder such as a polymerization inhibitor or a catalyst poison capable of reducing the polymerization rate of the olefin. However, the use of the retarder adversely affects the quality and the properties of the polymer, such as the melt index, the melt flow ratio, and/or the stereoregularity of the polymer, as well as decreasing the productivity of the process.

Moreover, in the gas-phase process there is formation of electrostatic charges. Therefore catalyst and resin particles tend to adhere to the reactor walls, as a result of the electrostatic forces. If the polymer remains in a reactive environment for a long time, excess temperature can result in particle fusion with the formation of sheets or layers of thin fused agglomerates in the granular product. There are numerous causes for the formation of electrostatic charges, including generation due to friction of dissimilar materials, limited static dissipation, introduction to the process of minute quantities of prostatic agents, excessive catalyst activities, etc. There is a strong correlation between sheeting and the presence of excessive electrostatic charges (either negative or positive). This is evidenced by sudden changes in electrostatic levels followed closely by deviation in temperature at the reactor wall. The temperature deviations indicate particle adhesion, which causes an insulating effect and poorer heat transfer from the bed temperature. As a result, there is generally disruption in the fluidization patterns, catalyst feed interruption can occur, as well as plugging at the product discharge system.

As discussed in U.S. Patent 4,532,311, the art teaches various processes whereby electrostatic charges can be

reduced or eliminated. Processes suitable for use in a fluidized bed include (1) the use of an additive to increase the conductivity of the particles, thus providing a path for electrical discharge, (2) installation of grounding devices in a fluidized bed, (3) ionization of gas or particles by electrical discharge to generate ions to neutralize electrostatic charges on the particles, and (4) the use of radioactive sources to produce radiation that will create ions to neutralize electrostatic charges on the particles. However, the application of such techniques to a commercial scale polymerization reactor using a fluidized bed usually is not feasible or practical.

In U.S. Patent 4,803,251 a group of chemical additives is disclosed which generate either positive or negative charges in the reactor and which are fed to the reactor in an amount of a few ppm per part of the monomer in order to prevent the formation of undesired positive or negative charges. The chemical additives include alcohols, oxygen, nitric oxide, and ketones. Also in this case, however, there is a resulting deterioration in the polymer quality as well as a decrease in the reactor productivity.

The above drawbacks are increased when a gas-phase polymerization process is carried out using a highly active-catalyst intended to produce spherical polymers having attractive morphological characteristics (high bulk density, flowability, and mechanical resistance). In this case, only a substantially complete control of the polymerization process enables one to obtain polymer particles having the above-desired characteristics. This is particularly true when the gas-phase process is used to produce ethylene polymers, wherein the high polymerization kinetic of ethylene exacerbates the problem.

See also EP-A 0416379 A2, which discloses a process for preparing thermoplastic olefin polymers wherein the polymerization is carried out in at least two reactors using a catalyst based on a titanium halide supported on active MgCl_2 . Reference is made to the possible precontacting of the preformed catalyst with small amounts of an olefin prior to the main polymerization step which is carried out in the liquid or gaseous phase.

Summary of the Invention

It has now been found that it is possible to carry out a gas-phase polymerization process in a smooth and reliable manner, overcoming or markedly reducing the above difficulties, without a sacrifice in specific productivity and/or a deterioration in polymer quality.

In particular, it has been found that it is possible to obtain ethylene and propylene polymers in the form of high bulk density flowable spherical particles using spheriform catalysts endowed of high activity. (By "spheriform" we mean substantially spheroidal or spherical particles.)

The process of the invention therefore offers the possibility, particularly with respect to the use of super-active catalysts having a specific activity of from 10 to 100 Kg/h of polymer per g of solid catalyst component and particle dimensions in the range of 30 to 150 μm , which catalyst cannot be used in other existing gas-phase processes, of obtaining spheriform polymers. Such spheriform polymers can be sold without the need of pelletization, which operation, as is known, is expensive in terms of energy consumption.

Further, the possibility of carrying out the gas-phase polymerization process with high specific productivity allows for a remarkable reduction in reactor volume.

Another advantage offered by the present process results from the nature of the prepolymer used, because the start up of the gas-phase reactor does not need any "bed resin" or initial dispersing bed, as is usually done in gas-phase processes of the prior art.

The continuous process of the present invention comprises the following steps:

a) contacting the catalyst components in the absence of polymerizable olefin or optionally in the presence of said olefin in an amount up to 3 g per g of solid catalyst component to form a stereospecific catalyst capable of polymerizing propylene under the conditions of step b) to form a propylene polymer having an insolubility in xylene of at least 60% by weight;

b) prepolymerizing with the above catalyst, propylene or mixtures thereof with minor amounts of ethylene and/or other alpha olefins of the formula $\text{CH}_2=\text{CHR}$ in which R is an alkyl with 1 to 8 carbon atoms such as butene-1, hexene, 4-methylpentene-1 to form a propylene polymer having an insolubility in xylene greater than 60%, preferably greater than 90%, in an amount of from 5 g polymer per g of solid catalyst component to 10% by weight of the final catalyst yield; and

c) polymerizing one or more olefins in the gas-phase in one or more reactors having a fluidized or mechanically agitated bed in the presence of the prepolymer-catalyst system formed in b) while circulating in the reactor or reactors an alkane having from 3 to 5 carbon atoms in a molar concentration in the gas-phase of from 20 to 90% with respect to the total gases.

Surprisingly and unexpectedly, the preforming of the catalyst, the prepolymerization treatment with the catalyst, and the presence of the alkane in the gas-phase in the molar concentration as indicated above, permits close control

of the gas-phase polymerization process, even under those conditions in which the prior art processes were unable to operate.

Detailed Description

In step a) the catalyst forming components are normally contacted with a liquid inert hydrocarbon solvent such as, e.g., propane, n-hexane or n-heptane, at a temperature below 60°C and preferably from 0° to 30°C for a time period of from six seconds to 60 minutes.

The catalyst forming components used in step a) include:

1) A solid comprising a titanium compound containing at least one Ti-halogen bond supported on active Mg-dihalide. The solid also contains an electron donor compound (inside donor) when the catalyst in itself is not sufficiently stereospecific to produce in step b) propylene polymers with the xylene insolubility characteristic set forth in b). As is known in the art, the stereospecificity of catalysts supported on active Mg-dihalide is increased by the use of an inside donor. As a general rule, the inside donor is always used when the catalyst component is employed to prepare catalysts for the stereoregular polymerization of propylene, butene-1 and similar alpha olefins in which a high stereospecificity is needed in order to obtain polymers with an Isotacticity Index higher than 90, preferably higher than 95.

2) An Al-alkyl compound.

3) Optionally an electron donor compound (outside donor) which may be the same or different from the one present in solid component 1). When the gas-phase process is used to produce stereoregular polymers, for instance, propylene polymers with a high isotacticity index, the outside donor is used to impart the catalyst the necessary high stereospecificity. However, when ethers of the type described in EP-A-344755 are used as the inside donor, the catalyst stereospecificity is in itself sufficiently high that no outside donor is needed. In the case of the polymerization of ethylene to produce HDPE (high density polyethylene), LLDPE (linear low density polyethylene) and similar polymers, an outside donor is used if the catalyst itself exhibits a stereospecificity insufficient to produce in step b) a propylene polymer with the xylene insolubility set forth therein.

The use in step b) of stereospecific catalysts allows one to obtain propylene polymers having, in addition to the insolubility in xylene indicated in b), a high intrinsic viscosity, i.e., greater than 1 dl/g, which high viscosity is important to impart to the prepolymer the desired morphological properties.

The catalyst formed in step a) is fed continuously or intermittently to step b).

Step b) can be carried out in the liquid or gas phase. Preferably it is carried out in the liquid phase, either using propylene itself as the liquid medium or using a hydrocarbon solvent such as n-hexane, n-heptane, cyclohexane or a low boiling alkane such as propane, butane (kept in the liquid state under the conditions used in b)).

Normally the polymerization of propylene in step b) is carried out at a temperature of from 0° to 80°C, preferably from 5° to 50°C. Propylene or mixtures of propylene with ethylene and/or other alpha olefins such as butene-1, hexene-1, 4-methylpentene-1, are polymerized to form polymers having an insolubility in xylene greater than 60%. The amount of the prepolymer formed ranges from 5 g polymer per g of the catalyst component to 10% by weight of the final catalyst yield, and preferably is from 5 g per g to 3% by weight of the final catalyst yield. The final catalyst yield can be determined by the analysis of the catalyst residues, for instance, from the titanium and/or magnesium content or from the balance of the materials.

Step b) can be carried out continuously or intermittently. In the case of continuous operation and when the gas-phase process is run to produce ethylene polymers, an appropriate separator system of the unreacted propylene is provided before feeding the prepolymer-catalyst system of step b) to the gas-phase reactor.

When the process is used to produce HDPE with a broad MWD (molecular weight distribution), it may be convenient to remove the outside donor present before feeding the prepolymer-catalyst system to the gas-phase reactor.

The gas-phase polymerization of step c) is carried out according to known techniques, operating in one or more reactors in cascade having a fluidized or mechanically agitated bed. The process is normally carried out at a temperature below the sintering temperature of the polymer particles. Generally the temperature is from 50° to 120°C, and more preferably from 70° to 100°C.

The total pressure is normally between 1.5 and 3 MPa. As previously indicated, the gaseous phase present in the reactor(s) contains an inert C₃-C₅ alkane in an amount of from 20 to 90% molar with respect to the total gases. Suitable alkanes include propane, butane, isobutane, n-pentane, isopentane, cyclopropane, or cyclobutane. Preferably the alkane is propane.

Normally the alkane is fed into the reactor either with the monomer or separately and is recycled with the recycle gas, i.e., the gas stream which does not react in the bed and which is removed from the polymerization zone, preferably by passing it into a velocity reduction zone above the bed where entrained particles are given an opportunity to drop

back into the bed. The recycle gas is then compressed and thereafter passed through a heat exchanger wherein it is stripped of heat of reaction before it is returned to the bed. See, e.g., U.S. Patents 3,298,792 and 4,518,750 for a description of gas-phase reactors and techniques.

It is surprising and completely unexpected that the alkanes are effective in providing the advantages as hereabove indicated, whereas the use of an inert gas like nitrogen is ineffective. Indeed, the use of nitrogen does not prevent the formation of large aggregates ("chunks"), with the consequent need to shut down the operation.

According to a preferred embodiment, the polymerization reaction is carried out in at least two reactors in cascade, in the first of which, wherein the initial amount of polymer is formed, the alkane concentration is maintained at a level higher than the concentration in the second (or subsequent reactors). Usually it is preferred that the alkane is circulated only in the first reactor wherein from 5 to 60% of the total polymer is produced. Conversely, in cases such as the sequential polymerization of propylene to produce impact propylene copolymers by 1) homopolymerization of propylene and 2) copolymerization of mixtures of ethylene and propylene, it is desirable to operate the process using substantially the same alkane concentration in the various reactors.

In the reactors the fluidization is normally achieved by using a high rate of gas recycle to and through the bed, typically of the order of about 50 times the rate of feed of make-up gas. Make-up gas is fed to the bed at a rate equal to the rate at which particulate polymer product is withdrawn.

To insure complete fluidization, the recycle gas and, where desired, part or all of the make-up gas normally are returned to the reactor at a point below the bed. A gas distribution plate positioned above the point of return ensures proper gas distribution and also supports the resin bed when gas flow is stopped.

Hydrogen may be used as a chain transfer agent to regulate the polymer molecular weight.

A typical simplified flow diagram of the process is given in accompanying FIG. 1. Reference numeral 1 indicates the pre-contacting vessel. The loop reactor 2 is the prepolymerizer. The gas-phase reactors are designated by 4 and 6, and the solid/gas separators are designated by 3, 5 and 7.

The catalyst components and diluent (propane) are fed to vessel 1 as indicated by arrows A. The formed catalyst is fed to loop reactor 2 as indicated by arrow B. Propylene is fed to the loop reactor as indicated by arrow E. The catalyst-prepolymer product is passed to separator 3, and then to the gas-phase reactor 4, wherein the monomer, hydrogen and propane are fed, as indicated by arrow C, to the recycle-gas line. The polymer leaving reactor 4, after passing through the separator 5, is introduced into the reactor 6, wherein the monomer, hydrogen and propane are fed as indicated by arrow D. The particulate polymer product is withdrawn from reactor 6 and fed to separator 7.

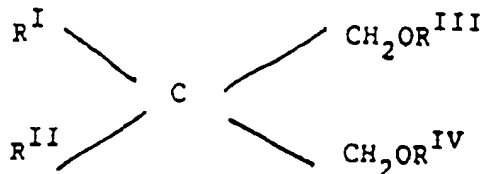
The active Mg-dihalides used as support for Ziegler-Natta catalysts are described extensively in the patent literature. U.S. Patents 4,298,718 and 4,495,338 described for the first time the use of said supports.

The Mg-dihalides forming the support of the catalyst components used in the process of the present invention are characterized by X-ray spectra wherein the most intense line which appears in the spectrum of the non-active halide is no longer present, but is substituted by a halo with the maximum intensity shifted towards lower angles with respect to the angle of the most intense line, or this line is still present but it appears broader.

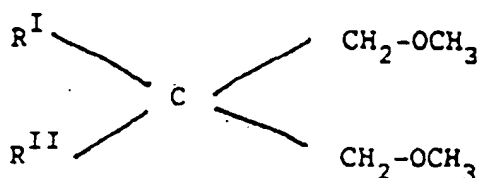
The titanium compounds suitable for the preparation of the solid catalyst component include Ti-halides such as TiCl_4 , which is the most preferred, TiCl_3 , and haloalcoholates such as trichlorophenoxy titanium and trichlobutoxy titanium.

The titanium compound can be used in mixtures with other transition metal compounds such as vanadium, zirconium and hafnium halides and haloalcoholates.

Suitable inside electron-donors include ethers, esters, amines, ketones, and diethers of the general formula



wherein R^{I} and R^{II} are the same or different from each other and may be alkyl, cycloalkyl and aryl radicals with 1 to 18 carbon atoms, and R^{III} and R^{IV} are the same or different and are alkyl radicals with from 1 to 4 carbon atoms. Preferred are the alkyl, cycloalkyl and aryl esters of polycarboxylic acids such as phthalic and maleic acid, and diethers of the formula



in which R^I and R^{II} are as above defined. Examples of said compounds include di-n-butyl phthalate, diisobutylphthalate, di-n-octyl-phthalate, 2-methyl-2-isopropyl-1,3 dimethoxy propane, 2-methyl-2- isobutyl-1,3-dimethoxypropane, 2,2-di-isobutyl-1,3- dimethoxypropane, 2-isopropyl-2-iso-pentyl-1,3-dimethoxypropane.

The internal donor is generally present in molar ratios with respect to the Mg of from 1:8 to 1:14. The titanium compound, expressed as Ti, is present in an amount of from 0.5 to 10% by weight.

Solid catalyst components can be prepared according to the disclosures of U.S. Patents 4,748,221 and 4,803,251. If the stereospecificity of the resulting catalyst is not sufficiently high for the purposes of this invention, it can be readily modified according to well known techniques as previously indicated.

Using catalysts obtained from the catalyst components described in EP-A-344 755 it is possible to prepare spherical polymers with an average diameter between 300 and 5000 μm , and in the case of ethylene and propylene polymers, a bulk density higher than 0.45 g/cm^3 .

The Al-alkyl compound used as the co-catalyst to prepare the catalyst in step a) may be an Al-trialkyl such as, e. g., Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, Al-tri-n-octyl. Mixtures of Al-trialkyls with Al-alkyl halides or Al-alkyl sesquihalides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$ may also be used. The Al/Ti ratio in the catalyst formed in a) is greater than 1 and generally is between 20 and 800.

The outside donor may be the same or different from the electron donor compound present as the inside donor.

When the internal donor is an ester of a polycarboxylic acid, especially a phthalate, the external donor is preferably a silicon compound of the formula $\text{R}_1\text{R}_2\text{Si}(\text{OR})_2$, where R_1 and R_2 are alkyl, cycloalkyl or aryl radicals with 1 to 18 carbon atoms. Preferably the silicon compounds are selected among dimethoxydialkyl and alkylcycloalkyl silanes. Examples of such silanes are methylcyclohexyldimethoxysilane, diphenyldimethoxy-silane, and methyl-t-butyl dimethoxysilane.

The solubility in xylene of the propylene polymer formed in step b) is determined by dissolving 2 g polymer in 250 ml xylene at 135°C while agitating. After 20 minutes the solution is left to cool until it reaches 25°C. After 30 minutes the precipitate material is filtered, the solution is evaporated in nitrogen gas, and the residue is dried under vacuum at 80°C. Thus, the percentage of polymer soluble in xylene at room temperature, and therefore also the insoluble percentage, are calculated.

As previously indicated, the process of this invention makes it possible to obtain a large number of different grades of olefin polymers, for example, high density polyethylenes (HDPE; density greater than 0.940), including homopolymers of ethylene and copolymers of ethylene with α -olefins having from 3 to 12 carbon atoms; linear low-density polyethylenes (LLDPE; density less than 0.940); and very low and ultra low density linear polyethylenes (VLLDPE and ULLDPE; density less than 0.920 and as low as 0.880) consisting of copolymers of ethylene and one or more α -olefins having from 3 to 12 carbon atoms, with a content of units derived from ethylene of over 80% by weight; elastomeric terpolymers of ethylene, propylene and dienes, and elastomeric copolymers of ethylene and propylene, having a content of units derived from ethylene comprised between about 30 and 70% by weight; isotactic polypropylenes and crystalline copolymers of propylene and ethylene and/or other α -olefins, having a content of units derived from propylene of over 85% by weight; impact polymers of propylene obtained by sequential polymerization of propylene and mixtures of propylene with ethylene, containing up to 30% by weight of ethylene; copolymers of propylene and butene-1 having a content of units derived from butene-1 comprised between 10 and 40% by weight.

As previously pointed out, the process is particularly suitable for the production of ethylene polymers wherein the high polymerization kinetic of ethylene requires a close control of the gas-phase process in order to avoid those difficulties typical of the prior art gas-phase processes, particularly when the process is carried out with high specific productivity.

As indicated, in the case of the polymerization of propylene or its mixture with ethylene and/or other olefins of the formula $\text{CH}_2=\text{CHR}$ to form stereoregular polymers, a highly stereospecific catalyst is needed. The highly stereospecific catalyst (capable of forming propylene homopolymers with an isotacticity index higher than 90) is preferably formed only in step b). If necessary the stereospecificity can be further modified by feeding proper quantities of an electron-donor compound into the polymerization reactor.

The following examples will further illustrate our invention. All parts are by weight unless otherwise indicated.

GENERAL PROCEDURE

The solid catalyst component used in the examples is prepared as follows.

Under an inert atmosphere, 28.4 g MgCl_2 , 49.5 g of anhydrous ethanol, 10 ml of ROL OB/30 vaseline oil, 100 ml of silicone oil having a viscosity of 350 cs are introduced into a reaction vessel equipped with a stirrer and heated at 120°C until the MgCl_2 is dissolved. The hot reaction mixture is then transferred to a 1,500 ml vessel equipped with a Ultra Turrax T-45 N stirrer and containing 150 ml of vaseline oil and 150 ml of silicone oil. The temperature is maintained at 120°C with stirring for 3 minutes at 3,000 rpm. The mixture is then discharged into a 2 liter vessel equipped with a stirrer containing 1,000 ml anhydrous n-heptane cooled at 0°C and stirred at a speed of 6 m/sec for about 20 minutes while maintaining the temperature 0°C. The particles thus formed are recovered by filtering, washed with 500 ml aliquots of n-hexane and heated gradually by increasing the temperature from 50°C to 100°C for a period of time sufficient to reduce the alcohol-content from 3 mole to the moles indicated in the various examples.

The adduct (25 g), containing the various alcohol content indicated in the examples, is transferred in a reaction vessel equipped with a stirrer and containing 625 ml of TiCl_4 at 0°C under agitation. It is then heated to 100°C in one hour. When the temperature reaches 40°C, diisobutylphthalate is added in an amount such that the molar ratio of Mg to the phthalate is 8. The contents of the vessel are then heated at 100°C for two hours with agitation and then the solid is allowed to settle. The hot liquid is removed by syphon. 500 ml of TiCl_4 are added and the mixture heated at 120°C for one hour with agitation. The agitation is stopped and the solid is allowed to settle. The hot liquid is removed by syphon. The solid is washed with aliquots of n-hexane at 60°C and then at room -temperature.

EXAMPLE 1

A pilot plant operated continuously is used to prepare LLDPE. The plant comprises a reaction vessel in which the catalyst-forming components are mixed to form the catalyst, a loop reactor receiving the catalyst formed in the previous stage and in which liquid propylene and propane are fed, and two fluidized-bed reactors connected in series, the first of which receives the prepolymer formed in the previous stage and discharges the polymer in the second reactor. These reactors are of the type described in U.S. Patent 4,518,750.

The run is carried out by feeding a solid catalyst component prepared according to the general procedure hereabove set forth using a MgCl_2 ethanol adduct containing 35% by weight alcohol, an n-hexane solution of Al-triethyl (TEAL) and methyl cyclohexyldimethoxysilane electron donor in an amount such that the weight ratio of TEAL to silane is 4 and the molar ratio TEAL/Ti is 120, into the activation vessel, which is kept at constant temperature of 5°C. In this vessel propane is also fed as an inert polymerization medium. The residence time is about 15 minutes.

The product discharged from the vessel is fed into the loop prepolymerizer kept at a constant temperature of 27°C. The residence time in the loop reactor is about 140 minutes. Due to both the low amount of propylene fed and the high conversion, the liquid propylene is almost completely converted into solid polymer (with a yield, referred to the solid catalyst component, of about 100 g/g solid component). The quantity of propylene entering the gas phase reactor is, therefore, negligible.

The first reactor, which receives the prepolymer produced in the previous step, runs at a temperature of 80°C and the reaction pressure is kept at 2 MPa.

The average residence time of the growing polymer inside the reactor is about 80 minutes.

The reaction monomers and the gas fed into the reactors, are the following:

- ethylene and butene;
- hydrogen as molecular weight regulator;
- propane.

PRECONTACT STAGE

5 - temperature (°C) = 5
 - residence time (min) = 15

PREPOLYMERIZATION STAGE

10 - temperature (°C) = 27
 - residence time (min) = 140

1ST GAS-PHASE REACTOR

15 - temperature (°C) = 80
 - pressure (MPa) = 2.0
 - residence time (min) = 80
 - ethylene (%mol) = 32.13 (**)
 - hydrogen (%mol) = 9.46 (**)
 - butene (%mol) = 6.43 (**)
 - propane (%mol) = 47.50 (**)

2ND GAS-PHASE REACTOR

25 - temperature (°C) = 80
 - pressure (MPa) = 1.5
 - residence time (min) = 60
 - ethylene (%mol) = 52.00 (**)
 - hydrogen (%mol) = 15.60 (**)
 - butene (%mol) = 11.33 (**)
 - propane (%mol) = 13.50 (**)

FINAL PRODUCT CHARACTERISTICS

35 - real density (Kg/l) = 0.9181 on pellets
 - melt index "E" (g/10') = 0.84 on pellets
 - poured bulk density (Kg/l) = 0.351
 - tamped bulk density (Kg/l) = 0.388
 - particle size: d > 2000 μ m (%wt) = 53.7 (*)
 - d > 1000 μ m (%wt) = 42.5 (*)
 - d > 500 μ m (%wt) = 3.6 (*)
 - d < 500 μ m (%wt) = 0.2 (*)
 - final mileage (kg PE/g solid
 catalyst component) = 33

45 NOTE: (*) d means diameter of the spherical form product
 obtained.

 (**) The complement to 100% being due to other inerts
 (ethane, butane, etc.) present in the monomers
 - fed.

EXAMPLE 2

55 HDPE is prepared using the plant arrangement described in Example 1.

The run is carried out by feeding the catalyst, components in the activation vessel which is kept at a constant temperature of 20°C. The product discharged from the vessel is fed into a loop prepolymerizer into which liquid propylene and propane (as inert medium) are also fed.

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The residence time in prepolymerization is about 82 minutes and the temperature is kept constant at 20°C.

The fluid contained in this prepolymerization reactor is in liquid state.

The liquid propylene is almost completely converted to solid polypropylene with a yield with the respect to the solid catalyst component of about 400 grams of polypropylene per gram of catalyst. The residual quantity of propylene discharged with the polymer from the prepolymerizer is flashed in order to have negligible quantities of propylene fed to the gas phase reactor.

The first reactor, which receives the prepolymer produced in the previous step, runs at a temperature of 75°C and the reaction pressure is kept at 1.8 MPa.

The average residence time of the growing polymer inside the reactor is about 96 minutes.

The reaction monomers and the gas fed into the reactor are the following:

- ethylene;
- hydrogen as molecular weight regulator;
- propane

PRECONTACT STAGE

5 - temperature (°C) = 20
 - residence time (min) = 15

PREPOLYMERIZATION STAGE

10 - temperature (°C) = 20
 - residence time (min) = 82

1ST GAS-PHASE REACTOR

15 - temperature (°C) = 75
 - pressure (MPa) = 1.8
 - residence time (min) = 96
 - ethylene (% mol) = 23 (**)
 - hydrogen (% mol) = 29 (**)
 - propane (% mol) = 40 (**)

2ND GAS-PHASE REACTOR

20 - temperature (°C) = 80
 - pressure (MPa) = 1.5
 - residence time (min) = 83
 - ethylene (% mol) = 23 (**)
 - hydrogen (% mol) = 30 (**)
 - propane (% mol) = 37 (**)

FINAL PRODUCT CHARACTERISTICS

30 - real density (kg/l) = 0.958
 - melt index "E" (g/10') = 4.5
 - poured bulk density (kg/l) = 0.403
 - tamped bulk density (kg/l) = 0.450
 - particle size: d > 2000 μm (% wt) = 77.1 (*)
 d > 1000 μm (% wt) = 22.2 (*)
 d > 500 μm (% wt) = 0.4 (*)
 d < 500 μm (% wt) = 0.3 (*)
 - final mileage (kg PE/g solid
 catalyst component = 40

NOTE: (*) d means diameter of the spherical form product
 obtained.

(**) the complement to 100% being due to other inerts
 (ethane, butane, ...) eventually present into the
 monomers fed.

EXAMPLE 3

The run is carried out by feeding a catalyst prepared according to Example 1, and batch prepolymerized with propylene directly in a single gas-phase reactor.

The temperature of the gas-phase reactor is 80°C and the pressure is 2 MPa.

The gas components fed to the reactor are the following:

- ethylene and butene

- hydrogen as molecular weight regulator
- propane

At the beginning, before feeding the prepolymerized catalyst to the gas-phase reactor, the propane concentration in the gas-phase is kept at about 60% molar. A smooth run is performed with the above propane concentration.

Decreasing the propane concentration below 30% molar results in the formation of large aggregates due to the very high reactivity inside the gas-phase reactor.

The run conditions in the smooth test are reported as follows:

PREPOLYMERIZED CATALYST

-mileage (KgPP/g solid catalyst compound) = 0.050

1ST GAS-PHASE REACTOR

- temperature	(°C)	=	80
- pressure	(MPa)	=	2.0
- ethylene	(% mol)	=	52 (*)
- hydrogen	(% mol)	=	7
- butene	(% mol)	=	6.5 (*)
- propane	(% mol)	=	32 (*)

NOTE: (*) The balance to 100% being due to other inerts (ethane, butane, etc.) present in the monomers fed.

COMPARATIVE EXAMPLE 1

A test for producing linear low density polyethylene is carried out as follows:

- catalyst activation stage;
- gas-phase polymerization stage.

The prepolymerization step is omitted in order to investigate both the influence of this step in controlling the polymer morphology and process reliability.

The activation vessel is run at a temperature of 30°C and the residence time is kept constant at 15 minutes.

The solid catalyst component (prepared according to the procedure of Example 1), the co-catalyst (TEAL), and the electron-donor (methylcyclohexyldimethoxysilane) are fed to the activation vessel with some added -propane (as inert medium) which permits one either to modify or to better control the residence time.

The discharged product is then fed to the first polymerization reactor which is kept at constant temperature of 75°C and the pressure is 1.8 MPa.

After about 30 minutes, the run has to be stopped because of the formation of some large aggregates (chunks) which disturb the proper functioning of the system.

After degassing and purging, a check of the internal of the gas-phase reactor shows the presence of chunks and formation of large crusts on the internal of the gas-phase reactor.

Before shutdown, the gas-phase reactor gives the composition reported in the following table (the run conditions of this trial are also reported):

ACTIVATION STAGE

5	- temperature	(°C)	=	20
	- residence time	(min)	=	15

1ST GAS-PHASE REACTION STAGE

10	-temperature	(°C)	=	75
	-pressure	(MPa)	=	1.8
	-residence time	(min)	=	n.d.
	-ethylene	(% mol)	=	5 (*)
	-hydrogen	(% mol)	=	1.5 (*)
	-butene	(% mol)	=	0.5 (*)
15	-propane	(% mol)	=	93

NOTE: (*) these values refer to in the initial composition
in the gas-phase reactor.

EXAMPLE 4

The test is carried out by using the following plant arrangement:

- activation stage;
- prepolymerization stage;
- gas phase polymerization stage (the polymerization is performed by using two gas-phase reactors connected in series).

The run is carried out by precontacting a solid catalyst component, Al-triethyl and methylcyclohexyldimethoxy silane in the ratio used in Example 1 in the activation vessel, which is kept at a constant temperature of 40°C. The catalyst component is prepared from a MgCl₂ ethanol adduct containing 50% by weight alcohol.

In this vessel propane is also fed, as inert reaction medium, and the resulting residence time is about 13 minutes.

The product discharged from the vessel is fed into a prepolymerizer into which propylene and propane (as inert medium) are also fed.

The residence time in prepolymerization is about two minutes and the temperature is kept constant at 20°C.

The fluid contained in this prepolymerization reactor is in a liquid state.

The gas-phase reaction section comprises two gas-phase reactors connected in series.

The first reactor, which receives the prepolymer produced in the previous step, runs at a temperature of 80°C and the reaction pressure is kept at 2.4 MPa.

The reaction monomer and gas fed into the reactor are the following:

- propylene
- hydrogen as molecular weight regulator
- propane

The run conditions are reported in the following table:

ACTIVATION STAGE

- temperature (°C) = 40
 - residence time (min) = 13

PREPOLYMERIZATION STAGE

- temperature (°C) = 20
 - residence time (min) = 2

1ST GAS-PHASE REACTOR

- temperature (°C) = 80
 - pressure (MPa) = 2.4
 - residence time (min) = 54
 - propylene (% mol) = 50.5 (**)
 - hydrogen (% mol) = 6.4 (**)
 - propane (% mol) = 41 (**)

2ND GAS-PHASE REACTOR

- temperature (°C) = 80
 - pressure (MPa) = 2.4
 - residence time (min) = 66
 - propylene (% mol) = 78.2 (**)
 - hydrogen (% mol) = 10.4 (**)
 - propane (% mol) = 5.5 (**)

FINAL PRODUCT CHARACTERISTICS

- poured bulk density (kg/l) = 0.472
 - tamped bulk density (kg/l) = 0.528
 - particle size: d > 2000 μm (% wt) = 21.9 (*)
 d > 1000 μm (% wt) = 66.3 (*)
 d > 500 μm (% wt) = 10.2 (*)
 d < 500 μm (% wt) = 1.6 (*)
 - final mileage (kgPP/g solid catalyst component) = 21.2

NOTE: (*) d means diameter of the spherical form product obtained.

(**) The complement to 100% being due to other inerts (methane, ethane, etc.) present into the monomers fed.

In all of the examples carried out in accordance with the present invention, the pilot plant runs smoothly with full control of all operating conditions.

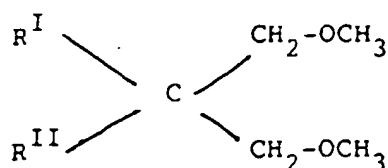
Variations can of course be made without departing from the spirit of our invention.

Claims

1. A continuous process for the gas-phase polymerization and copolymerization of olefins of the formula $\text{CH}_2=\text{CHR}$ where R is hydrogen or an alkyl or aryl radical with 1 to 8 carbon atoms using a catalyst comprising the product of reaction of the following components (1) a Ti compound containing at least a Ti-halogen bond and optionally an

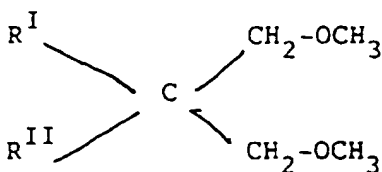
electron-donor compound supported by an active Mg-dihalide with (2) an Al-trialkyl compound and optionally an electron donor compound, this process comprising:

- a) contacting the catalyst components in the absence of polymerizable olefin or optionally in the presence of said olefin in an amount up to 3 g per g of solid catalyst component to form a stereospecific catalyst capable of polymerizing propylene under the conditions of step b) to form a propylene polymer having an insolubility in xylene of at least 60% by weight;
 - b) prepolymerizing with the above-formed catalyst propylene or mixtures of propylene with minor amounts of ethylene and/or an alpha-olefin with 4 to 8 carbon atoms to form a propylene polymer having an insolubility in xylene higher than 60% by weight in an amount of from 5 g polymer per g solid catalyst component to 10% by weight of the final catalyst yield;
 - c) polymerizing one or more olefins of the formula $\text{CH}_2=\text{CHR}$ in the gas phase in one or more reactors having a fluidized or mechanically agitated bed with the aid of the prepolymer-catalyst system obtained in b), said polymerization reaction being carried out in the presence of an alkane having from 3 to 5 carbon atoms, the molar concentration of the alkane with respect to the total gases being from 20 to 90%.
2. The process of claim 1 wherein the polymerization is carried out in two reactors, in the first of which from 5 to 60% by weight of the total polymer is produced, and wherein the concentration of alkane is higher in the first reactor than in the second reactor.
 3. The process of claim 2 wherein the catalyst prepared in step a) contains both an inside and an outside electron-donor compound.
 4. The process of claim 3 wherein the inside donor is an ester of phthalic acid and the outside donor is a dimethoxy dialkyl or alkylcycloalkyl silane.
 5. The process of claim 1 or 2 wherein the catalyst formed in b) contains as an inside donor a diether of the formula



in which R^{I} and R^{II} may be the same or different and are alkyl, cycloalkyl or aryl radicals with 1 to 18 carbon atoms.

6. The process of claim 4 or 5, wherein a spheriform catalyst is used, the specific activity of which is from 10 to 100 Kg per hour per gram of solid catalyst component and the average particle diameter of which is between 30 and 150 microns.
7. The process of claim 1 or 2 wherein the alkane is propane.
8. The process of claim 3 wherein the alkane is propane.
9. A process of claim 4 wherein the alkane is propane.
10. The process of claim 1 or 2 wherein the catalyst is prepared using an outside donor and a spheriform solid component containing an inside donor, and wherein the alkane is propane.
11. The process of claim 1 or 2 wherein the catalyst is obtained from a spheriform solid component containing as an inside donor a diether of formula



in which R^I and R^{II} may be the same or different and are alkyl, cycloalkyl or aryl radicals with 1 to 18 carbon atoms, and wherein the alkane used is propane.

12. Spheriform polymers of ethylene obtainable by the process of claim 1 or 2, characterized by an average diameter comprised between 300 and 5000 μm .
13. Spheriform polymers of propylene obtainable by the process of claim 10, characterized by an average diameter comprised between 300 and 5000 μm and a bulk density higher than 0.45 g/cm^3 .
14. Spheriform polymers of propylene obtainable by the process of claim 11, characterized by an average diameter comprised between 300 and 5000 μm and a bulk density higher than 0.45 g/cm^3 .

Patentansprüche

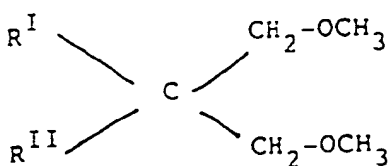
1. Kontinuierliches Verfahren zur Gasphasenpolymerisation und -copolymerisation von Olefinen der Formel $\text{CH}_2 = \text{CHR}$, worin R Wasserstoff oder ein Alkyl- oder Arylrest mit 1 bis 8 Kohlenstoffatomen ist, unter Verwendung eines Katalysators, der das Reaktionsprodukt der folgenden Komponenten umfaßt (1) einer Ti-Verbindung, die wenigstens eine Ti-Halogenbindung und gegebenenfalls eine Elektronendonatorverbindung trägergestützt auf einem aktiven Mg-Dihalogenid enthält, mit (2) einer Al-Trialkylverbindung und gegebenenfalls einer Elektronendonatorverbindung, wobei das Verfahren umfaßt:

a) Kontaktieren der Katalysatorkomponenten in Abwesenheit von polymerisierbarem Olefin oder gegebenenfalls in Anwesenheit des Olefins in einer Menge bis zu 3 g pro g der festen Katalysatorkomponente zur Bildung eines stereospezifischen Katalysators, der zur Polymerisation von Propylen unter den Bedingungen der Stufe b) in der Lage ist, um ein Propylenpolymeres mit einer Unlöslichkeit in Xylol von wenigstens 60 Gewichts-% zu bilden;

b) Vorpolymerisation mit dem oben gebildeten Katalysator von Propylen und Gemischen von Propylen mit kleineren Mengen an Ethylen und/oder einem α -Olefin mit 4 bis 8 Kohlenstoffatomen zur Bildung eines Propylenpolymeren, das eine Unlöslichkeit in Xylol von mehr als 60 Gewichts-% hat, in einer Menge von 5 g Polymeres pro g feste Katalysatorkomponente bis 10 Gewichts-% der finalen Katalysatorausbeute;

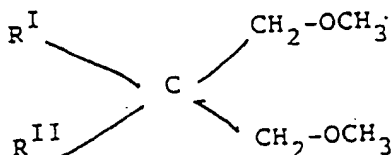
c) Polymerisation von einem oder mehreren Olefinen der Formel $\text{CH}_2 = \text{CHR}$ in der Gasphase in einem oder mehreren Reaktoren, die ein Fließbett oder mechanisch gerührtes Bett aufweisen, mit Hilfe des in b) erhaltenen Vorpolymer-Katalysatorsystems, wobei die Polymerisationsreaktion in Gegenwart eines Alkans durchgeführt wird, das 3 bis 5 Kohlenstoffatome hat, wobei die molare Konzentration des Alkans im Hinblick auf das Gesamtgas 20 bis 90 % beträgt.

2. Verfahren nach Anspruch 1, worin die Polymerisation in zwei Reaktoren durchgeführt wird, wobei in dem ersten von 5 bis 60 Gewichts-% des Gesamtpolymeren hergestellt wird und wobei die Konzentration des Alkans in dem ersten Reaktor höher ist als in dem zweiten Reaktor.
3. Verfahren nach Anspruch 2, worin der in Stufe a) hergestellte Katalysator eine innere und eine äußere Elektronendonatorverbindung enthält.
4. Verfahren nach Anspruch 3, worin der Innendonator ein Ester der Phthalsäure ist, und der Außendonator ist ein Dimethoxydialkyl- oder -alkylcycloalkylsilan.
5. Verfahren nach Anspruch 1 oder 2, worin der in b) gebildete Katalysator als Innendonator einen Diether der Formel



enthält, worin R^I und R^{II} gleich oder verschieden sein können und Alkyl-, Cycloalkyl- oder Arylreste mit 1 bis 18 Kohlenstoffatomen sind.

6. Verfahren nach Anspruch 4 oder 5, worin ein kugeltartiger Katalysator verwendet wird, dessen spezifische Aktivität von 10 bis 100 kg pro Stunde pro Gramm feste Katalysatorkomponente beträgt und dessen durchschnittlicher Teilchendurchmesser zwischen 30 und 150 Mikrometer liegt.
7. Verfahren nach Anspruch 1 oder 2, worin das Alkan Propan ist.
8. Verfahren nach Anspruch 3, worin das Alkan Propan ist.
9. Verfahren nach Anspruch 4, worin das Alkan Propan ist.
10. Verfahren nach Anspruch 1 oder 2, worin der Katalysator unter Verwendung eines Außendonators und einer kugeltartigen festen Komponente, die einen Innendonator enthält, hergestellt wird, und worin das Alkan Propan ist.
11. Verfahren nach Anspruch 1 oder 2, worin der Katalysator aus einer kugeltartigen festen Komponente erhalten wird, die als einen Innendonator einen Diether der Formel



enthält, worin R^I und R^{II} gleich oder verschieden sein können und Alkyl-, Cycloalkyl- oder Arylreste mit 1 bis 18 Kohlenstoffatomen sind, und worin das verwendete Alkan Propan ist.

12. Kugeltartige Polymere von Ethylen, erhältlich durch das Verfahren von Anspruch 1 oder 2, gekennzeichnet durch einen durchschnittlichen Durchmesser, der zwischen 300 und 5000 µm liegt.
13. Kugeltartige Polymere von Propylen, erhältlich durch das Verfahren nach Anspruch 10, gekennzeichnet durch einen durchschnittlichen Durchmesser, der zwischen 300 und 5000 µm liegt, und durch eine Schüttdichte von höher als 0,45 g/cm³.
14. Kugeltartige Polymere von Propylen, erhältlich durch das Verfahren nach Anspruch 11, gekennzeichnet durch einen durchschnittlichen Durchmesser, der zwischen 300 und 5000 µm liegt, und durch eine Schüttdichte von höher als 0,45 g/cm³.

Revendications

1. Un procédé continu de polymérisation et de copolymérisation en phase gazeuse d'oléfines de formule CH₂=CHR dans laquelle R est un atome d'hydrogène ou un radical alkyle ou aryle comportant 1 à 8 atomes de carbone, en utilisant un catalyseur comprenant le produit de la réaction des constituants suivants :

- 1) un dérivé de titane comportant au moins une liaison Ti-halogène et, le cas échéant, un composé électrodonneur supporté sur un dihalogénure de magnésium activé avec;
- 2) un dérivé trialkylaluminium et, le cas échéant, un dérivé électrodonneur;

ce procédé comprenant :

a) la mise en contact des constituants catalytiques en l'absence d'oléfines polymérisables ou éventuellement en présence desdites oléfines en une quantité pouvant atteindre 3 g par gramme de constituant catalytique solide en donnant un catalyseur stéréospécifique capable de polymériser le propylène dans les conditions de l'étape b) en donnant un polymère de polypropylène présentant une insolubilité dans le xylène d'au moins 60% en poids;

b) la prépolymérisation à l'aide du catalyseur préparé ci-dessus, de propylène ou de mélanges de propylène avec des quantités mineures d'éthylène et/ou d'alpha-oléfines comportant 4 à 8 atomes de carbone, pour former un polymère de propylène présentant une insolubilité dans le xylène supérieure à 60% en poids, en une quantité comprise entre 5 g de polymère par gramme de constituant catalytique solide et 10% en poids du rendement final du catalyseur; et

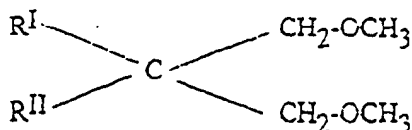
c) la polymérisation d'une ou plusieurs oléfines de formule $\text{CH}_2=\text{CHR}$ en phase gazeuse dans un ou plusieurs réacteurs renfermant un lit fluidisé ou agité mécaniquement à l'aide du système prépolymère/catalyseur formé en b) ladite réaction de polymérisation étant effectuée en présence d'un alcane comportant de 3 à 5 atomes de carbone, la concentration molaire de l'alcane par rapport la quantité totale de gaz étant de 20 à 90%.

2. Le procédé selon la revendication 1, dans lequel on effectue la polymérisation dans deux réacteurs, dans le premier réacteur on obtient 5 à 60% en poids de la quantité totale de polymère, et dans lequel la concentration en alcane est plus élevée dans le premier réacteur que dans le second réacteur.

3. Le procédé selon la revendication 2, dans lequel le catalyseur préparé dans l'étape a) contient à la fois un composé électrodonneur interne et un composé électrodonneur externe.

4. Le procédé selon la revendication 3, dans lequel le composé donneur interne est un ester de l'acide phtalique et le composé donneur externe est un di-méthoxydialkyl-silane ou un alkylcycloalkyl-silane.

5. Le procédé selon la revendication 1 ou 2, dans lequel le catalyseur formé en b) contient, en tant que donneur interne, un diéther de formule :



dans laquelle :

R^{I} et R^{II} , identiques ou différents, sont des radicaux alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone.

6. Le procédé selon la revendication 5 ou 6, dans lequel on utilise un catalyseur sphériforme, dont l'activité spécifique est de 10 à 100 kg par heure par gramme de constituant catalytique solide et dont le diamètre particulaire moyen est compris entre 30 et 150 μm .

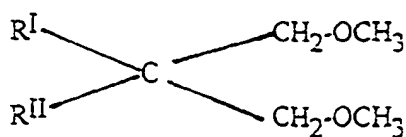
7. Le procédé selon la revendication 1 ou 2, dans lequel l'alcane est le propane.

8. Le procédé selon la revendication 3, dans lequel l'alcane est le propane.

9. Un procédé selon la revendication 4, dans lequel l'alcane est le propane.

10. Le procédé selon la revendication 1 ou 2, dans lequel on prépare le catalyseur en utilisant un composé donneur externe et un constituant solide sphériforme contenant un donneur interne et dans lequel l'alcane est le propane.

11. Le procédé selon la revendication 1 ou 2, dans lequel on obtient le catalyseur à partir d'un constituant solide sphériforme contenant, en tant que donneur interne, un diéther de formule :



dans laquelle :

R^{I} et R^{II} , identiques ou différents, sont des radicaux alkyle, cycloalkyle ou aryle, comportant 1 à 18 atomes de carbone,

et dans lequel l'alcane utilisé est le propane.

12. Polymères sphériformes d'éthylène préparables par un procédé selon la revendication 1 ou 2, caractérisés en ce qu'ils ont un diamètre moyen compris entre 300 et 5000 μm .
13. Polymères sphériformes de propylène préparables par un procédé selon la revendication 10, caractérisés en ce qu'ils présentent un diamètre moyen compris entre 300 et 5000 μm et une densité apparente supérieure à 0,45 g/cm^3 .
14. Polymères sphériformes de propylène préparables par un procédé selon la revendication 11, caractérisés en ce qu'ils présentent un diamètre moyen compris entre 300 et 5000 μm et une densité apparente supérieure à 0,45 g/cm^3 .

